Title: The Aqueous Thermodynamics and Complexation Reactions of Anionic Silica and Uranium Species to High Concentration.

Project Number: 30944

Name of Laboratory: Pacific Northwest National Laboratory

PNNL Principal Investigator: ANDREW R. FELMY

Problem Statement and Research Objective

Highly basic tank wastes contain several important radionuclides, including ^{90}Sr, ^{99}Tc, and ^{60}Co, as well as actinide elements (i.e., isotopes of U, Pu, and Am). These highly basic tank wastes are known to have leaked into the vadose zone at the Hanford Site. In particular, wastes from the bismuth phosphate process contained very high concentrations of U as well as carbonate, phosphate, nitrate, and other components (AEC 1951) and these solutions have leaked into the subsurface at the Hanford site. The tanks containing the bismuth phosphate wastes were frequently saturated with respect to the solid phases of these components [e.g., $NaUO_2PO_4(c)$ and $Na_4UO_2(CO_3)_3(c)$]. These solids were referred to as "hard sludge" ($Na_4UO_2(CO_3)_3(c)$) and "soft sludge" [$NaUO_2PO_4(c)$] because of their different crystal forms. The preliminary studies of the solubility of these solids in tank wastes (AEC 1951) indicate that aqueous U carbonate complexes dominate the solution chemistry of uranium even when the equilibrium solid was $NaUO_2PO_4$. Thus there was a need to develop an accurate thermodynamic model for the solubility of potentially important U(VI) phosphate and carbonate phases as well as to develop a model for the uranium carbonate complexes valid to high ionic strength.

In this project we are examining the solubility of these important solid phases as well as the aqueous thermodynamics of U(VI) species under strongly basic conditions. Also included is a description of our efforts to include these thermodynamic models in the reactive transport and residual leaching models being used at the Hanford site and elsewhere.

Research Progress and Implications

The Solubility of the $(UO_2)_3(PO_4)_2.4H_2O$ and $(PuO_2)_3(PO_4)_2.4H_2O$

When we first initiated the uranium studies the issue of the stability of the normal phosphate $(UO_2)_3(PO_4)_2.4H_2O$ and the stability of sodium uranium phosphate ($NaUO_2PO_4.xH_2O$) was of concern. In particular, there appeared to be a discrepancy in the reported solubility products reported for the normal phosphate. This apparent discrepancy in solubility products was one of the motivating factors in our initial studies focused on the solubility of the normal phosphate $(UO_2)_3(PO_4)_2.4H_2O$ and the analogous Pu(VI) system.

The objectives of the normal phosphate studies were to address uncertainties in both the solubility product of $(UO_2)_3(PO_4)_2.4H_2O(c)$and in the phosphate complexes of U(VI), and to ascertain the extent to which U(VI) and Pu(VI) behave in an analogous fashion. Studies were conducted on $(UO_2)_3(PO_4)_2.4H_2O(c)$ and $(PuO_2)_3(PO_4)_2.4H_2O(c)$ solubilities for long equilibration periods over a wide range of pH values (2.5 to 10.5) at fixed phosphate

concentrations of 0.001 and 0.01 M, and in a range of phosphate concentrations (0.0001 to 1.0 M) at fixed pH values of about 3.5. A combination of techniques (X-Ray Diffraction (XRD), thermogravimetric analysis (TGA) and X-Ray Absorption Spectroscopy (XAS)) was used to characterize the reaction products. A comprehensive thermodynamic model for $(PuO_2)_3(PO_4)_2.4H_2O$ solubility in the H^+-Na^+-OH^--Cl^--$H_2PO_4^-$-HPO_4^{2-}-PO_4^{3-}-H_2O system, previously unavailable, was also presented and the data shows that the U(VI)-phosphate system is an excellent analog for the Pu(VI)-phosphate system. These studies have recently been published (Rai et al., 2005).

The Development of Pitzer Ion-interaction Parameters for U(VI)-Carbonate Complexes

We have also calculated accurate values for the Pitzer ion-interaction parameters for the important Na^+ interactions with $UO_2(CO_3)_3^{4-}$ and $(UO_2)_3(CO_3)_6^{6-}$ as well as the mixing parameters for the $UO_2(CO_3)_3^{4-}$ species with sulfate and chloride. These data are essential for developing a model to describe the ionic strength dependence of any aqueous complex containing the $UO_2(CO_3)_3^{4-}$ moiety. The best set of data for evaluating the Pitzer ion-interaction parameters for the $UO_2(CO_3)_3^{4-}$ complex was the extensive solubility data for ĉejkaite given by Blake et al., (1956) They measured the solubility of ĉejkaite in several different electrolytes to high ionic strength and at least partially verified that the dominant species present in solution was the tricarbonate complex ($UO_2(CO_3)_3^{4-}$) generated by the stoichiometric dissolution reaction of ĉejkaite,

$$Na_4UO_2(CO_3)_3 = 4Na^+ + UO_2(CO_3)_3^{4-}. \quad (1)$$

In analyzing the data of Blake et al., (1956) we initially determined the Na^+ - $UO_2(CO_3)_3^{4-}$ ion-interaction parameters from the ĉejkaite solubility data in $NaClO_4$ media. The data in $NaClO_4$ were chosen since it is expected that the ClO_4^- anion will be a relatively weakly interacting anion and the majority of the non-ideal aqueous thermodynamics will be captured in the strong binary Na^+ - $UO_2(CO_3)_3^{4-}$ interactions. The resulting analysis also yielded new values for the Pitzer ion interaction parameters [β^0 (Na^+ - $UO_2(CO_3)_3^{4-}$) = 0.61 and β^1 (Na^+ - $UO_2(CO_3)_3^{4-}$ = 18.2]. For completeness, we fit the solubility data in the NaCl and Na_2SO_4 systems and then tested the final parameterizations in the mixed NaCl-Na_2CO_3 system using only the parameters from the simpler systems.

Also of importance in this study of the U(VI) carbonate and phosphate complexation was our application of the Liquid Helium Temperature Laser Fluorescence (LHeT) technique. LHeT analysis allows us to identify the presence of both the metal-U(VI)-carbonate complexes and the uncomplexed U(VI)-carbonate species. Previous fluorescence studies at room temperature of the Ca-U(VI)-carbonates could not identify the presence of the uncomplexed U(VI)-carbonates. This lack of information on the $UO_2(CO_3)_3^{4-}$ species in the complexation reaction,

$$2Ca^{2+} + UO_2(CO_3)_3^{4-} = Ca_2UO_2(CO_3)_3(aq) \quad (2)$$

is a clear source of uncertainty in determining the importance of this complexation reaction. These studies were completed and are accepted (Felmy et al., 2005, accepted).

Development of Reactive Transport and Tank Waste Residual Release Models

One of the major contributions of this project has been the incorporation and use of our thermodynamic models in other applications. Specifically, we have supplied the necessary computer code (several subroutines from our GMIN software used for thermodynamic predictions) to implement the Pitzer thermodynamic model in the subsurface reactive transport models being used to simulate the transport of contaminants in subsurface systems. The most recent thermodynamic databases, developed as part of this and other projects, were updated during the course of this study and supplied to subsurface modeling teams with whom we are collaborating. These teams included those of Peter Lichtner (Los Alamos National Laboratory), Steve Yabusaki (PNNL), and Carl Steefel (Lawrence Berkeley National Laboratory). As a result of these significant efforts, all of the thermodynamic data developed as part of this study can be used immediately in essentially all of the reactive transport modeling codes for simulations of the Hanford and other DOE sites.

In addition, to our activities at the Hanford site we have also been supporting other EMSP investigators in their research efforts including Professor Markus Flury at Washington State University and Professor Kathy Nagy at the University of Illinois. These collaborative studies have been examining basic concentrated leachates from sediments, or sediment fragments, from the Hanford site and have also resulted in two manuscripts so far (Mashal et al. 2004; Mashal et al. 2005, in review).

A summary of the publications supported by this project related to the uranium studies and implementation in reactive transport modeling follows.

- Mashal, K., J.B. Harsh, M. Flury, and A.R. Felmy. (2004). Colloid Formation in Hanford Sediments Reacted with Simulated Tank Waste. Environmental Science and Technology 38(21):5750-5756.
- Felmy, A.R., M.J. Mason, O. Qafoku, and D.A. Dixon. (2005). Development of Accurate Chemical Equilibrium Models for the Hanford Tanks: The System Na-Ca-Sr-OH-CO_3-NO_3-EDTA-HEDTA-H_2O. In. *Subsurface Contamination Remediation: Accomplishments of the Environmental Management Sciences Program.* ACS Symposium Series Vol 904.
- Felmy, A.R., Z. Wang, D.A. Dixon, and N.J. Hess. (2005). Chemical Equilibrium Modeling of Hanford Waste Tank Processing: Applications of Fundamental Science. In *Waste Management 04 Symposium. Basic Environmental Science Issues for D&D, ER and Long-Term Stewardship in the US*., in press.
- Rai, D., Y. Xia, L. Rao, N.J. Hess, A.R. Felmy, D.A. Moore, and D.E. McCready. (2005). Solubility of $(UO_2)_3(PO_4)_2.4H_2O$ in H^+-Na^+-OH^--$H_2PO_4^-$-HPO_4^{2-}-PO_4^{3-}-H_2O and its Comparison to the Analogous PuO_2^{2+} System. Journal of Solution Chemistry, 34 (4), 469-498.
- Mashal, K., J.B. Harsh, M. Flury, and A.R. Felmy. (2005). Analysis of Precipitates from Reaction of Hypersaline Solutions with Soluble Silica. Applied Geochemistry, 20, 1357-1367.
- Felmy, A.R., Y. Xia, and Z. Wang. (2005). The Solubility Product of $NaUO_2PO_4.xH_2O$ Determined in Phosphate and Carbonate Solutions. Radiochimica Acta, in press.